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| | | 1b. RESTRICTIVE MARKINGS | | | | | | | | | |
| | | 3. DISTRIBUTION/AVAILABILITY OF REPORT | | | | | | | | | |
| | | Approved for public release; distribution unlimited. | | | | | | | | | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S) | | 5. MONITORING ORGANIZATION REPORT NUMBER(S) | | | | | | | | | |
| | | ARO 22448.9-CH | | | | | | | | | |
| 6a. NAME OF PERFORMING ORGANIZATION | 6b. OFFICE SYMBOL (If applicable) | 7a. NAME OF MONITORING ORGANIZATION | | | | | | | | | |
| Univ. of Texas at Austin | | U. S. Army Research Office | | | | | | | | | |
| 6c. ADDRESS (City, State, and ZIP Code) | | 7b. ADDRESS (City, State, and ZIP Code) | | | | | | | | | |
| Austin, TX 78712 | | P. O. Box 12211 Research Triangle Park, NC 27709-2211 | | | | | | | | | |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION | 8b. OFFICE SYMBOL (If applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER | | | | | | | | | |
| U. S. Army Research Office | | DAAG29-85-K-0104 | | | | | | | | | |
| 8c. ADDRESS (City, State, and ZIP Code) | | 10. SOURCE OF FUNDING NUMBERS | | | | | | | | | |
| P. O. Box 12211 Research Triangle Park, NC 27709-2211 | | <table border="1"> <tr> <td>PROGRAM ELEMENT NO</td> <td>PROJECT NO.</td> <td>TASK NO.</td> <td>WORK UNIT ACCESSION NO</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> </tr> </table> | | PROGRAM ELEMENT NO | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO | | | | |
| PROGRAM ELEMENT NO | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO | | | | | | | | |
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| 11. TITLE (Include Security Classification) | | | | | | | | | | | |
| Electrogenerated Chemiluminescence | | | | | | | | | | | |
| 12. PERSONAL AUTHOR(S) | | | | | | | | | | | |
| Allen J. Bard | | | | | | | | | | | |
| 13a. TYPE OF REPORT | 13b. TIME COVERED | 14. DATE OF REPORT (Year, Month, Day) | 15. PAGE COUNT | | | | | | | | |
| Final | FROM 4/15/85 TO 4/14/88 | June 1988 | 9 | | | | | | | | |
| 16. SUPPLEMENTARY NOTATION | | | | | | | | | | | |
| The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation. | | | | | | | | | | | |
| 17. COSATI CODES | | 18. SUBJECT TERMS | | | | | | | | | |
| FIELD | GROUP | SUB-GROUP | | | | | | | | | |
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| | | Electrogenerated chemiluminescence, Metal Electrodes, Chemiluminescence, Electroluminescence, Micelle Systems, Semiconductor Electrodes | | | | | | | | | |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) | | | | | | | | | | | |
| <p>Electrogenerated chemiluminescence (ECL) has been investigated in a variety of systems under various conditions. Eleven completed publications plus one manuscript in preparation address the following areas:</p> <ol style="list-style-type: none"> 1. ECL of novel inorganic complexes. 2. ECL from peroxyoxalate/luminescer systems. 3. ECL in micelle systems. 4. ECL at polymer modified electrodes. 5. Electroluminescence at semiconductor electrodes. 6. ECL from systems containing no added luminescer. 7. Inverse photoemission from metal electrodes. | | | | | | | | | | | |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT | | 21. ABSTRACT SECURITY CLASSIFICATION | | | | | | | | | |
| <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS | | Unclassified | | | | | | | | | |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL | | 22b. TELEPHONE (Include Area Code) | 22c. OFFICE SYMBOL | | | | | | | | |
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SUMMARY OF RESULTS

We have investigated electrogenerated chemiluminescence (ECL) in a variety of systems under various conditions. Eleven completed publications plus one manuscript in preparation address the following areas:

1. ECL of novel inorganic complexes.
2. ECL from peroxyoxalate/luminescer systems.
3. ECL in micelle systems.
4. ECL at polymer modified electrodes.
5. Electroluminescence at semiconductor electrodes.
6. ECL from systems containing no added luminescer.
7. Inverse photoemission from metal electrodes

ECL of Novel Inorganic Complexes. Most previous ECL experiments employed aromatic compounds (e.g., rubrene) or mononuclear metal complexes containing chelating polypyridyl ligands (e.g., $\text{Ru}(\text{bpy})_3^{2+}$). However, there exists a variety of luminescent inorganic and organometallic compounds containing more than one metal center, whose ECL properties have not been widely studied. In addition to their relatively high quantum yield, the excited states possess metal-metal interactions and are inherently different from those of mononuclear complexes. We have investigated the ECL properties of several binuclear metal complexes, including Mo_2 , Pt_2 , and Ir_2 systems.

The electrochemistry and ECL properties of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ (abbr. Mo_2) have been studied in tetrahydrofuran (THF) and acetonitrile (CH_3CN).¹ At a Pt electrode in THF-TBABF₄, the complex undergoes a reversible 1 e⁻ oxidation and 1 e⁻ reduction at +0.60 and -1.78 V vs. Ag quasireference electrode. The Mo_2^- anion is relatively stable, while the Mo_2^+ cation undergoes a following chemical reaction with a rate constant of 4.0 s⁻¹. ECL is produced by pulsing the Pt electrode between the $\text{Mo}_2^{+/0}$ and $\text{Mo}_2^{0/-}$ potentials; emission results from the annihilation of Mo_2^+ and Mo_2^- . The ECL spectrum displays a band maximum at 680 nm, characteristic of the $^1(\delta\delta^*)$ excited state of the Mo(II)-Mo(II) d⁴-d⁴ chromophore. The ECL efficiency was determined to be ca. 0.002, significantly lower than the luminescence quantum yield of 0.13 determined in THF. This may be partially due to the instability of Mo_2^+ . The same ECL spectrum was obtained by reducing Mo_2 in the presence of $\text{S}_2\text{O}_8^{2-}$. Reduction of $\text{S}_2\text{O}_8^{2-}$ by Mo_2^- produces SO_4^\cdot , a strong oxidizing agent. Electron transfer between Mo_2^- and SO_4^\cdot produce the luminescent $^1(\delta\delta^*)$ excited state.

(1) J. Ouyang, T. C. Zietlow, M. D. Hopkins, R.-R. F. Fan, H. B. Gray, and A. J. Bard, *J. Phys. Chem.* **90**, 3841 (1986).

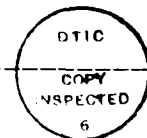
The binuclear Pt(II) complex, $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ (abbreviated Pt_2^{4-}) has attracted much attention for its long lived excited states and rich photochemistry. We studied the electrochemistry and ECL of this complex in $\text{CH}_3\text{CN}/\text{TBABF}_4$.² Pt_2^{4-} is irreversibly oxidized at +0.45 V vs. Ag quasireference electrode and is believed to be reduced at ca. -2.9 V, though this potential falls in the $\text{CH}_3\text{CN}/\text{TBABF}_4$ background. Rapid pulsing between these potential limits yields ECL, in which the emission maximum is centered at 512 nm. This is characteristic of the $^3(d\sigma^*p\sigma)$ excited state of the Pt(II)-Pt(II) d^8 - d^8 chromophore. However, it was found that the same ECL was produced by merely stepping the potential to the cathodic limit of the $\text{Pt}_2^{4-}/\text{CH}_3\text{CN}/\text{TBABF}_4$ solution. It is suggested that reduction of the TBA^+ cation occurs, generating the highly oxidizing butyl radical, which reacts via electron transfer with Pt_2^{5-} to give the luminescent excited state.

2. J. Kim, F.-R. F. Fan, A. J. Bard, C.-M. Che and H. B. Gray, *Chem. Phys. Letts.*, **121**, 543 (1985).

We have extended our studies of ECL from d^8 - d^8 complexes to compounds of the type $[\text{Ir}(\text{COD})(\mu\text{-L})_2]$ (abbreviated Ir_2), where COD=1,5-cyclooctadiene and L=bridging pyrazolyl ligands.³ The compounds offer the advantage of better defined, more reversible redox couples than those observed in $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ (see above). At a Pt electrode in THF/ TBAPF_6 solution, the Ir_2 complexes exhibit a reversible one electrode oxidation (+0.34 V vs. SCE for L=unsubstituted pyrazolyl) and a one electron reduction (-2.49 V vs. SCE for L=unsubstituted pyrazolyl).

While the Ir_2^+ species are fairly stable, the Ir_2^- cations undergo a following chemical reaction, the rate of which is inhibited by increasing substitution of the bridging pyrazolyl ligand. Sequential generation of Ir_2^+ and Ir_2^- at a Pt electrode yields ECL identical to the $^3(d\sigma^*d\sigma)$ emission observed in the photoluminescence spectra of the Ir_2 complexes. Identical ECL is obtained by oxidizing Ir_2 in the presence of $\text{C}_2\text{O}_4^{2-}$, where Ir_2^+ oxidizes $\text{C}_2\text{O}_4^{2-}$ to give the reducing species CO_2^- . Electron transfer between Ir_2 and CO_2^- probably gives rise to the luminescent Ir_2 species.

3. G. S. Rodman and A. J. Bard, manuscript in preparation.



We have directed our continuing interest in mononuclear metal complexes containing polypyridyl ligands towards developing compounds with enhanced ECL efficiency, as well as compounds with luminescence maxima significantly different from that of the prototypical complex $\text{Ru}(\text{bpy})_3^{2+}$. Such properties would be highly desirable in schemes utilizing ECL tags for detecting very dilute solution species and in multicomponent analysis. We studied the electrochemistry, excited state lifetime and ECL properties of $\text{Os}(\text{bpz})_3^{2+}$, where bpz =2,2'-bipyridine.⁴ This complex displays a reversible one electron

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oxidation at +1.52 V and three reversible one electron reductions at -0.67, -0.86, and -1.24 V (all potentials vs. SSCE in $\text{CH}_3\text{CN}(\text{TBAPF}_6)$). These waves correspond to the $\text{Os}^{3+/2+}$, $\text{Os}^{2+/+}$, $\text{Os}^{+/0}$, and $\text{Os}^{0/-}$ couples, respectively. The potentials for all the redox couples are shifted to more positive potentials than those of the parent $\text{Os}(\text{bpy})_3^{2+}$. ECL is observed when the working electrode was pulsed at 50 Hz between the anodic peak potential and the first cathodic peak potential. The ECL spectrum consists of a band centered at 700 nm, identical to the luminescence spectrum of $\text{Os}(\text{bpz})_3^{2+}$ (720 nm), and the excited lifetime of the bpz complex is significantly longer (0.24 μs vs. 0.02 μs for $\text{Os}(\text{bpy})_3^{2+}$, both in CH_3CN). The $\text{Os}(\text{bpz})_3^{2+}$ also exhibits a larger ECL efficiency than $\text{Os}(\text{bpy})_3^{2+}$ probably due to the enhanced lifetime of the luminescent excited state.

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4. C.-W. Lee, J. Ouyang, and A. J. Bard, *J. Electroanal. Chem.* **244**, 319 (1988).
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ECL from Oxalate Ester-Luminescer Systems. We have investigated the electrochemical behavior of bis(2,4,6-trichlorophenyl)oxalate (TCPO) and the ECL of TCPO-luminescer systems in acetonitrile/benzene (2:1 by volume) solution.⁵ This oxalate ester has been widely used in chemiluminescence studies because of its ease of preparation, stability, and high quantum yield, although the exact reaction mechanism has not been established. Conventional chemiluminescence applications of oxalate esters involve the use of hydrogen peroxide⁶ to generate the postulated key intermediate, 1,2-dioxetanedione, which reacts with added luminescer to give chemiluminescence. Thorough analysis of the processes leading to luminescence in the systems is complicated by the instability of oxalate esters in the presence of water and peroxide. Electrochemical generation of the reactive intermediate in nonaqueous solution appears to be a promising alternative method of studying the complex system.

TCPO undergoes a quasireversible, one electron reduction at -1.12 V vs. Ag quasireference electrode to give TCPO^- , stable only under rigorously O_2 -free conditions. In the presence of even minute amounts of O_2 , TCPO^- reacts rapidly with O_2 , which is produced concurrently at the Pt electrode under the conditions employed. The ultimate products of this reaction are CO_2 and trichlorophenoxide ion; the same products obtained by reacting TCPO and H_2O_2 . ECL is observed in TCPO solutions containing O_2 and a luminescer (such as 9,10-diphenylanthracene or $\text{Ru}(\text{bpy})_3^{2+}$) at potentials corresponding to TCPO and O_2 reduction. The resulting ECL spectrum is characteristic of the luminescer employed. No ECL is observed when oxygen is rigorously excluded under otherwise identical conditions. An unstable intermediate produced in TCPO- O_2 reduction is thought to react with the added luminescer to produce the observed luminescence. The use of TCPO in the electrochemical detection of trace amounts of O_2 by ECL is proposed.

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5. R. Brina and A. J. Bard, *J. Electroanal. Chem.*, **238**, 277 (1987).

6. K. Honda, K. Miyequchi, and K. Imai, *Anal. Chim. Acta.*, **177**, 103 (1985).
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ECL in Micelle Systems. We have investigated the microenvironmental effects of micelles on the electrochemical and ECL properties of $\text{Os}(\text{bpy})_3^{2+}$.⁷ This study was motivated by interest in applying trisbipyridyl complexes and other emitting centers as tags for analysis of species at low concentrations.⁸

In certain samples, particularly biological fluids, the addition of surfactants can be helpful in suppressing the effects of interference.

The oxidation electrochemistry and ECL behavior of $\text{Os}(\text{bpy})_3^{2+}$ was studied in the absence and presence of the different surfactants, sodium dodecyl sulfate (SDS), Triton X-100, and cetyltrimethylammonium bromide (CTAB) in aqueous solution. ECL was obtained by oxidizing $\text{Os}(\text{bpy})_3^{2+}$ /surfactant solutions containing oxalate. The luminescent species, $\text{Os}(\text{bpy})_3^{2+*}$, is generated by the reaction of $\text{Os}(\text{bpy})_3^{3+}$ and CO_2^- , a strongly reducing intermediate obtained upon oxidation of oxalate by $\text{Ru}(\text{bpy})_3^{3+}$.

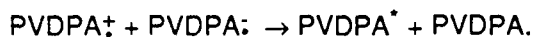
Large decreases in oxidative current and ECL intensity and decreases in the diffusion coefficient of $\text{Os}(\text{bpy})_3^{2+}$ were observed in the presence of SDS; only slight changes were observed in the presence of CTAB or Triton X-100. In the absence of SDS, the ECL maximum occurs at 730 nm. A significant red shift in the ECL spectrum ($\lambda_{\text{max}} = 765$ nm) occurred in the presence of SDS above the critical micelle concentration (CMC), while a smaller blue shift ($\lambda_{\text{max}} = 710$) was observed with SDS concentrations below the CMC. The wavelength of the ECL band observed above the CMC of SDS is similar to a low energy shoulder found in the emission spectrum of $\text{Os}(\text{bpy})_3^{2+}$ in apolar solvents. For example, in hexane, the emission spectrum of $\text{Os}(\text{bpy})_3^{2+}$ consists of a band centered at 720 nm with a shoulder at 767 nm. These observations are interpreted in terms of a strong interaction of $\text{Os}(\text{bpy})_3^{2+}$ with the hydrophobic core of the anionic SDS micelles, a strong interaction with SDS aggregates below the CMC, and weak or no interaction with the cationic surfactant CTAB or the neutral surfactant, Triton X-100.

7. J. Ouyang and A. J. Bard, *Bull. Chem. Soc. Jpn.*, **61**, 17 (1988).

8. D. Ege, W. G. Becker and A. J. Bard, *Anal. Chem.*, **56**, 2413 (1984).

ECL at Polymer Modified Electrodes. The electrochemical behavior of electrodes modified with thin layers of polymer has been a subject of intense activity over the last several years. The ECL technique may be employed to study electron transfer reactions and charge transfer in polymers containing suitable chromophores. In addition, we were interested in exploring the conformational changes that may occur within polymer coatings during the electron transfer reactions which give rise to ECL. Toward this end, we studied the electrochemistry, absorption, photoluminescence and ECL of poly(vinyl-9,10-diphenylanthracene) (PVDPA) thin films on various substrates in several solvents.⁹

The electrochemical and spectroscopic properties of spin-coated PVDPA films are similar to that of the monomer 9,10-diphenylanthracene (DPA), indicating that the multiple electroactive groups and chromophores in the polyvinyl chain do not interact strongly. The PVDPA films may be completely oxidized to PVDPA^+ by passing the electrode to a potential more positive than the anodic peak potential (+1.4 V vs. SCE in propylene carbonate). Similarly, the films may be completely reduced to PVDPA^- at potentials more negative than the cathodic peak potential (-1.9 V vs. SCE). ECL occurs upon stepping the electrode potential between +1.6 V and -2.0 V vs. SCE (100 ms pulse width) where oxidation and reduction of PVDPA occurs, respectively. The ECL spectrum of PVDPA is similar to the photoluminescence spectrum, suggesting that ECL occurs via the reaction of PVDPA^+ and PVDPA^- as shown below.



The photoluminescence and ECL spectra after several pulsing experiments display a new long wave component not seen in experiments carried out on fresh PVDPA films. These results suggest the formation of stable products produced by the decomposition of PVDPA^{\ddagger} and/or PVDPA^{\cdot} .

9 F.-R. F. Fan, A. Mau, and A. J. Bard, *Chem. Phys. Lett.*, **116**, 400 (1985).

Electroluminescence of Semiconductor Electrodes. Another type of ECL system that has become of special interest with the increasing activity in the area of semiconductor electrodes, involves the emission of light via electron-hole (e^-h^+) recombination at the surface of a semiconductor during electrolysis. For example, the reduction of $\text{S}_2\text{O}_8^{2-}$ at n-type ZnS, TiO_2 , CdSe, and other materials leads to emission when an electron in the semiconductor conduction band combines with a hole injected into the valence band by the electrogenerated SO_4^{\cdot} species (frequently via intermediate energy levels). A number of studies in this area have been reported by our group, as well as those of Gerischer, Memming, Ellis and others. This work is of importance because it provides a link between ECL and solid state electroluminescence (EL) and because studies of the emission can probe intermediate and surface state levels in a semiconductor electrode.

In continuing our work on ZnS systems, we studied the temperature dependence of the electroluminescence (in persulfate-butyronitrile solution) and the time resolved photoluminescence of Al-doped ZnS single crystals.¹⁰ Laser excitation of Al-doped ZnS gives a blue emission with a short lived exponential decay component lifetime of about ca. 3.7 ns) followed by a slow-decay component which obeys an approximate t^{-1} decay rate law. We have interpreted this slow decay by a model based on electron tunneling between two localized states (donor and acceptor) to generate an excited state. The excited state undergoes radiative recombination along with a thermally activated, non-radiative decay. Thermal deactivation of the excited state was demonstrated by measuring the temperature dependence of electroluminescence from the ZnS- $\text{S}_2\text{O}_8^{2-}$ system. Reduction of $\text{S}_2\text{O}_8^{2-}$ at ZnS electrodes generates the luminescent excited state via hole injection from the highly oxidizing intermediate SO_4^{\cdot} . The relative electroluminescence quantum yield decreases exponentially with increasing temperatures between 200 and 300 K, with an activation energy of 0.20 eV. Nonradiative decay may occur by the release of electrons from donor states to the conduction band or to nonradiative recombination centers. The observed activation barrier is thought to represent the energy required to promote an electron from the donor state to the conduction band, in agreement with previous measurements¹¹ of the ionization energy of donor states associated with Al-doped ZnS. The half-width of the electroluminescence spectrum was found to increase linearly with $T^{1/2}$, with the emission maximum unchanged over the temperature responsible for the luminescence takes place between two localized levels, rather than between an energy band and a localized level.

10. F.-R. F. Fan and A. J. Bard, *J. Phys. Chem.*, **89**, 1232 (1985).

11. H. A. Klasens, *J. Electrochem. Soc.* **100**, 72 (1953).

The photo- and electroluminescence properties of Mn-doped single crystal ZnS were examined along with the electroluminescence of polycrystalline, chemically vapor deposited (CVD) ZnS doped with Al, Al-Cu, and Mn.¹² The photoluminescence spectrum of Mn-doped ZnS single crystals gave a band centered at 580 nm, characteristic of the $4T_1 \rightarrow 6A_1$ transition in Mn^{2+} ions. The luminescence was partially quenched by modifying the semiconductor surface with I_2 -treated poly(vinylferrocene). Such quenching may be attributed to changes in the width of the space-charge region and in the rate of the electron-hole recombination at the Mn-ZnS surface.

Electroluminescence was observed upon reduction of $S_2O_8^{2-}$ at Mn-ZnS electrodes, by hole injection from the oxidizing intermediate $SO_4^{\cdot -}$. The spectrum was identical to that obtained in photoluminescence experiments. The electroluminescence intensity is sensitive to pH; a maximum is achieved at pH=ca. 8.5. In the region between pH 5 and 9, the variations in electroluminescence intensity can be explained by pH induced variations in the semiconductor flat-band potential. The temperature dependence of the Mn-ZnS- $S_2O_8^{2-}$ electroluminescence was studied between 200 and 300 K in butyronitrile. The luminescence intensity decrease with increasing temperature, with an activation energy of 0.14 eV.

In order to evaluate the ability of relatively inexpensive CVD semiconductors to give electroluminescence, CVD ZnS electrodes doped with Al, Cu or Mn were used to reduce $S_2O_8^{2-}$ solutions. Relatively efficient electroluminescence (ca. 0.2-0.3%) was observed, with the emission maxima in each case blue shifted from those observed in single crystal experiments. Thus CVD ZnS appears to be an excellent material for electroluminescence studies.

12. J. Ouyang, F.-R. F. Fan, and A. J. Bard, *J. Electrochem. Soc.*, submitted.

ECL from Acetonitrile Solutions Containing No Added Luminescers. Our interest in exploiting ECL as an analytical method for determining very low concentrations of luminescers⁸ has motivated us to investigate the low level detection limit, often governed by background emission processes. We have observed ECL from acetonitrile (CH_3CN) solutions containing only tetrabutylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte.¹³ When very negative potentials (< -3.5 V vs. Ag quasireference electrode) are applied to a Pt electrode in $CH_3CN/TBABF_4$, weak ECL is observed, with the emission centered at ca. 500 nm. At such potentials reduction of the solvent/electrolyte mixture occurs. The addition of $TBA_2S_2O_8$ produced a large (ca. 1-2 orders of magnitude) increase in ECL intensity at the same applied potentials; the resulting ECL spectrum is similar to that obtained from $CH_3CN/TBABF_4$. Under these conditions, reduction of $S_2O_8^{2-}$ occurs to yield the highly oxidizing $SO_4^{\cdot -}$ moiety.

Bulk electrolysis of an CH_3CN solution containing TBABF₄ and $TBA_2S_2O_8$ at -3.5 V formed a yellow film on the electrode surface and a yellow product in solution. The yellow material gave a luminescence spectrum with bands at 420 and 466 nm. Further analysis by IR, ¹H NMR, and X-ray photoelectron spectroscopy (XPS) suggest that the yellow material is polyacetonitrile, which is presumed to be responsible for the observed ECL. In the absence of added $TBA_2S_2O_8$, reduction of $CH_3CN/TBABF_4$ is

thought to produce polyacetonitrile along with butyl radicals (Bu^\bullet). Reaction of Bu^\bullet with a reduced form of polyacetonitrile is probably responsible for the observed ECL. The enhanced ECL from solutions containing $\text{S}_2\text{O}_8^{2-}$ is probably due to the more facile formation of polyacetonitrile by SO_4^\bullet oxidation of CH_3CN .

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13. J. Ouyang and A. J. Bard, *J. Electroanal. Chem.*, **222**, 33 (1987).
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Inverse Photoemission. Inverse photoemission (IP) involves light emission from a metal/electrolyte interface when an electron (or hole) is injected into a metal electrode. This weak emission is of interest because it sets the ultimate low limit of analytical determination by ECL, once all solution impurities and background ECL processes (such as those that occur in $\text{CH}_3\text{CN}/\text{TBABF}_4$ solutions¹³) are eliminated. In addition, IP spectroscopy promises to be a new and useful tool in probing the electrode/solution interface at lower energies than those required for conventional photoemission studies.

We have studied IP from Pt electrodes in $\text{CH}_3\text{CN}/\text{TBABF}_4$ solution when electrons¹⁴ or holes¹⁵ are injected from solution redox couples. In the case of IP via electron injection, IP is observed when upon oxidation of a stable anion radical at sufficiently positive potentials, characterized by E_{th} . By employing a series of ten compounds with standard reduction potentials ranging from -0.60 to -2.22 V vs. SCE, it was found that IP occurred only with those compounds having reduction potentials more negative than -1.90 V. $E_{\text{R,th}}$. The IP spectra exhibit a blue shift with increasingly negative reduction potentials and are unrelated to the luminescence spectra of the redox couples themselves. Various control experiments were performed to eliminate the possibility that the observed luminescence was due to background ECL processes. With benzophenone as the redox couple, the efficiency of IP was estimated to be ca. 10^{-7} , in line with theoretical predictions.¹⁶ Complementary results were obtained in a study employing ten compounds with standard potentials ranging from +0.22 to +1.44 V vs. SCE, again at a Pt electrode in $\text{CH}_3\text{CN}/\text{TBABF}_4$. Here, reduction of a stable cation radical at sufficiently negative potentials produces IP. It was found that IP is produced only with redox couples more positive than +1.0 V vs. SCE, designated $E_{\text{o,th}}$. The observation of a redox threshold for IP via hole injection ($E_{\text{o,th}}$) coupled to the threshold observed for electron injection ($E_{\text{R,th}}$) suggests a distribution of surface state energies spanning 2.9 eV at the $\text{Pt}/\text{CH}_3\text{CN}/\text{TBABF}_4$ interface. Electrons or holes injected at energies between $E_{\text{o,th}}$ and $E_{\text{R,th}}$ are most efficiently deactivated by nonradiative recombination of the electron-hole pair at a proposed Shockly-type surface state. Preliminary studies indicate IP from Rh electrodes is ca. five times weaker than that observed from Pt under the same conditions.

14. J. Ouyang and A. J. Bard, *J. Phys. Chem.* **91**, 4058 (1987).

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